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# Single-source precursors for $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> thin-films



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## Introduction

Photoelectrochemical water-splitting is one method of producing hydrogen from non-hydrocarbon primary energy sources. Photoelectrochemical water-splitting is often performed using metal oxide thin-films<sup>1</sup>, which ideally will have:

- A band-gap of suitable energy for efficient absorption of the solar spectrum
- A band-gap whose valence and conduction band energies bridge the redox potentials of the two relevant half-reactions:

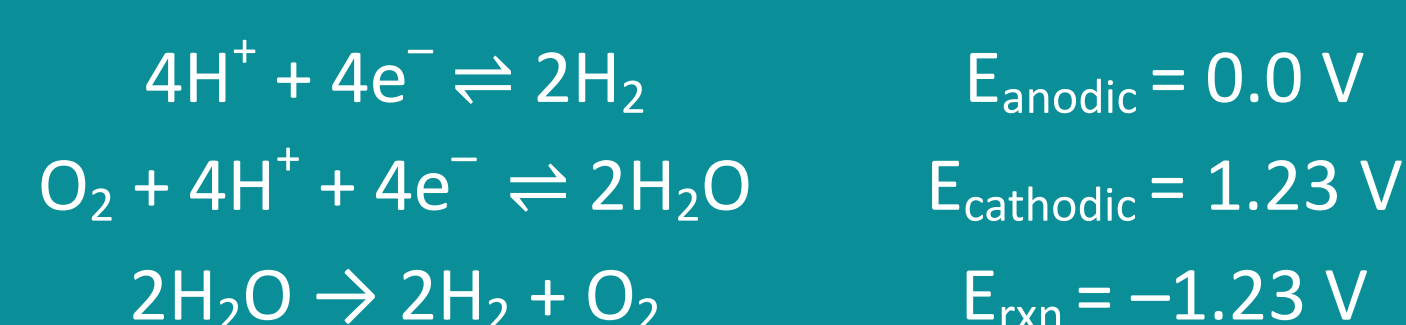


Fig. 1: Hydrogen-evolving devices can be manufactured from Fe<sub>2</sub>O<sub>3</sub> precursors

## Deposition of $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> thin-films

- $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> has a band-gap of 1.9–2.2 eV, making it a suitable photo absorber for water-splitting<sup>2</sup>
- Iron is earth-abundant and cheap, making hematite an inherently sustainable material.
- AA-CVD can be used to deposit a wide selection of single-source precursors.<sup>3</sup>

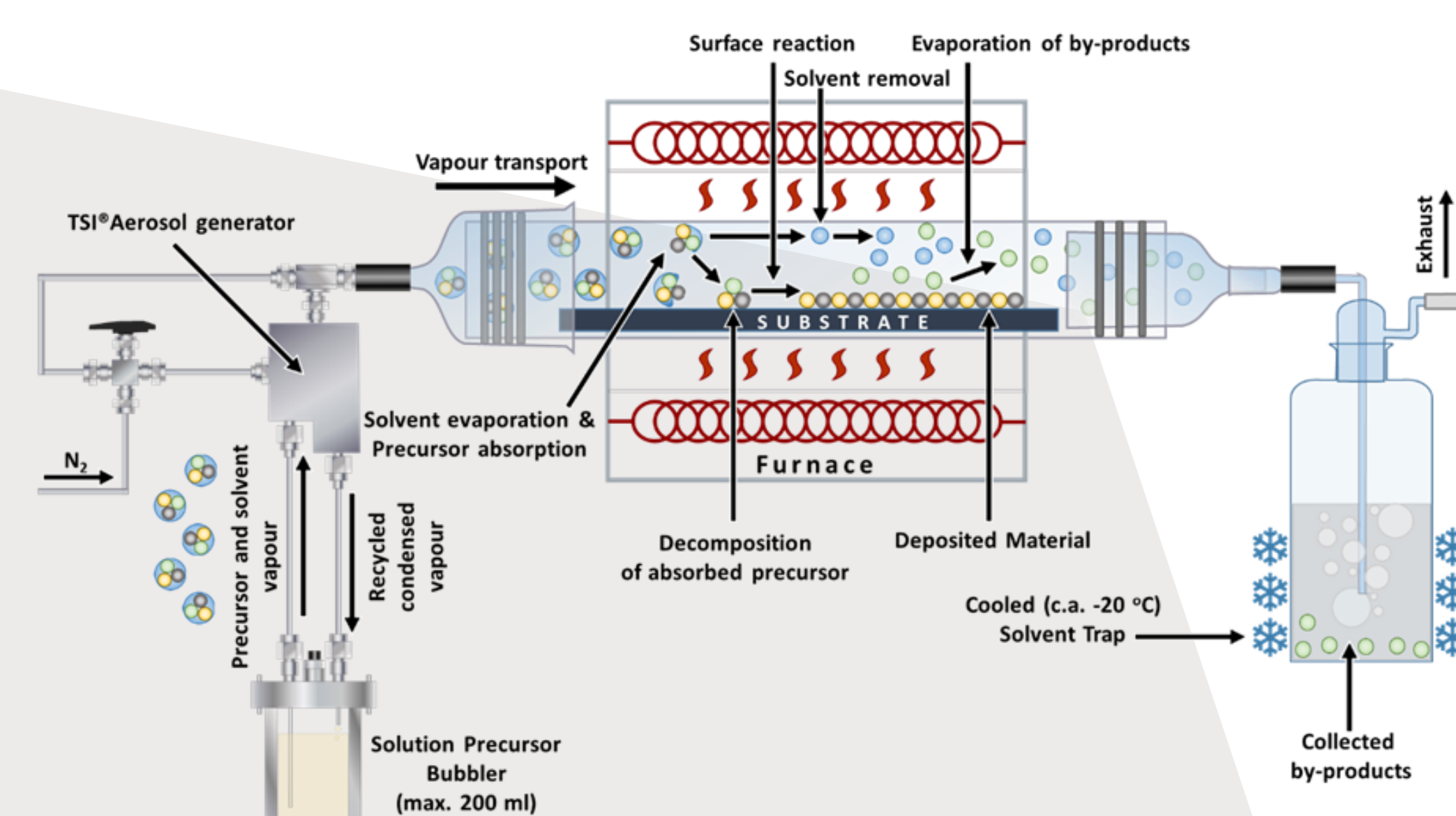
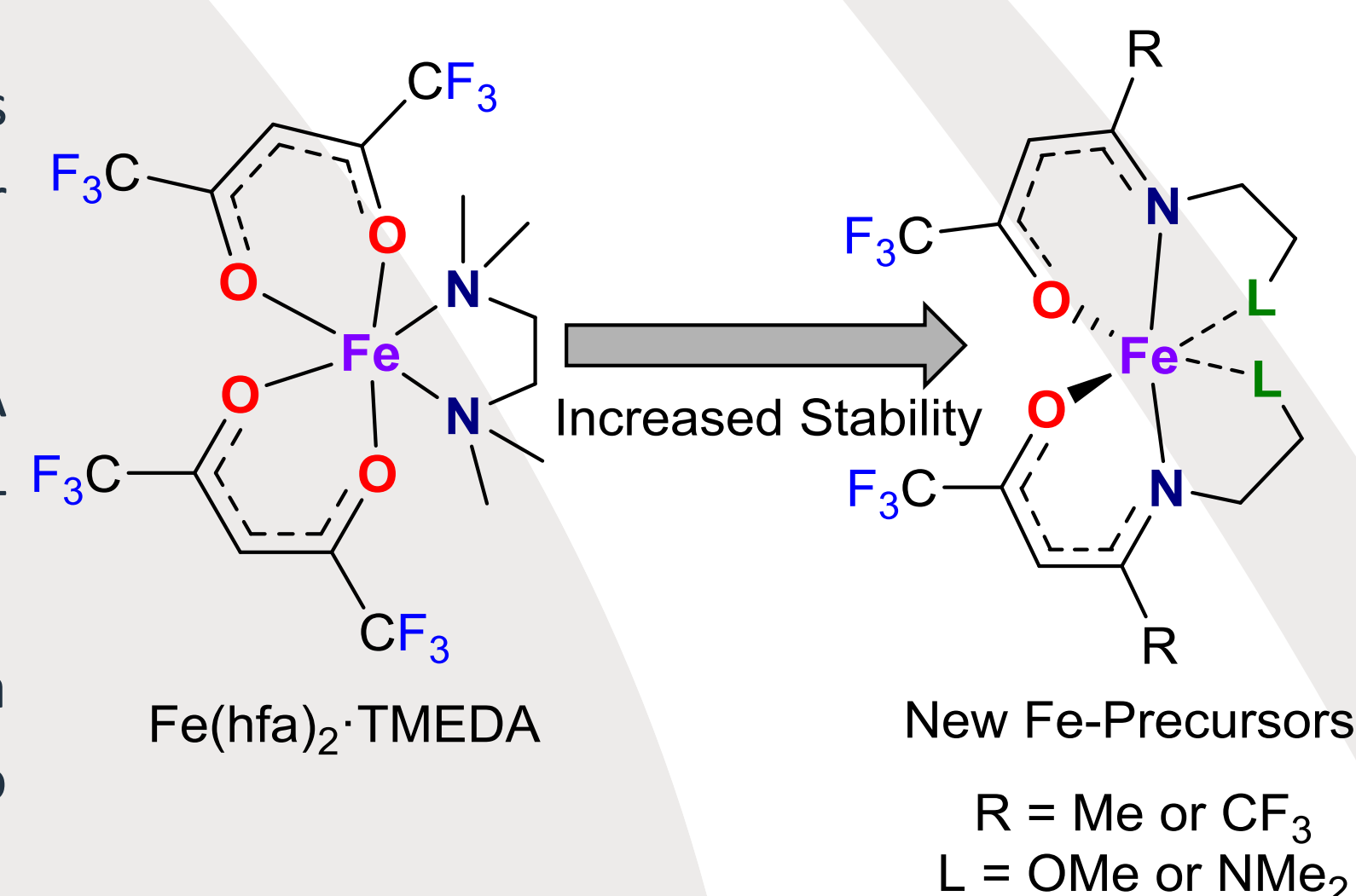


Fig. 2: Schematic of the aerosol-assisted chemical vapour deposition rig used

## Precursor design

- The iron complex Fe(hfa)<sub>2</sub>·TMEDA has been shown to be a useful precursor for the deposition of  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.<sup>4</sup>
- At elevated temperatures the TMEDA ligand is labile, making the precursor involatile.
- By modifying the {fac} ligands to bear a pendant donor group we may be able to increase the stability of precursors.



## $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> single-source precursors

- A series of iron (II) complexes have been synthesised as prospective single-source precursors to  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>.
- The molecular structure of several complexes have been determined by single crystal X-ray diffraction, and are shown below.

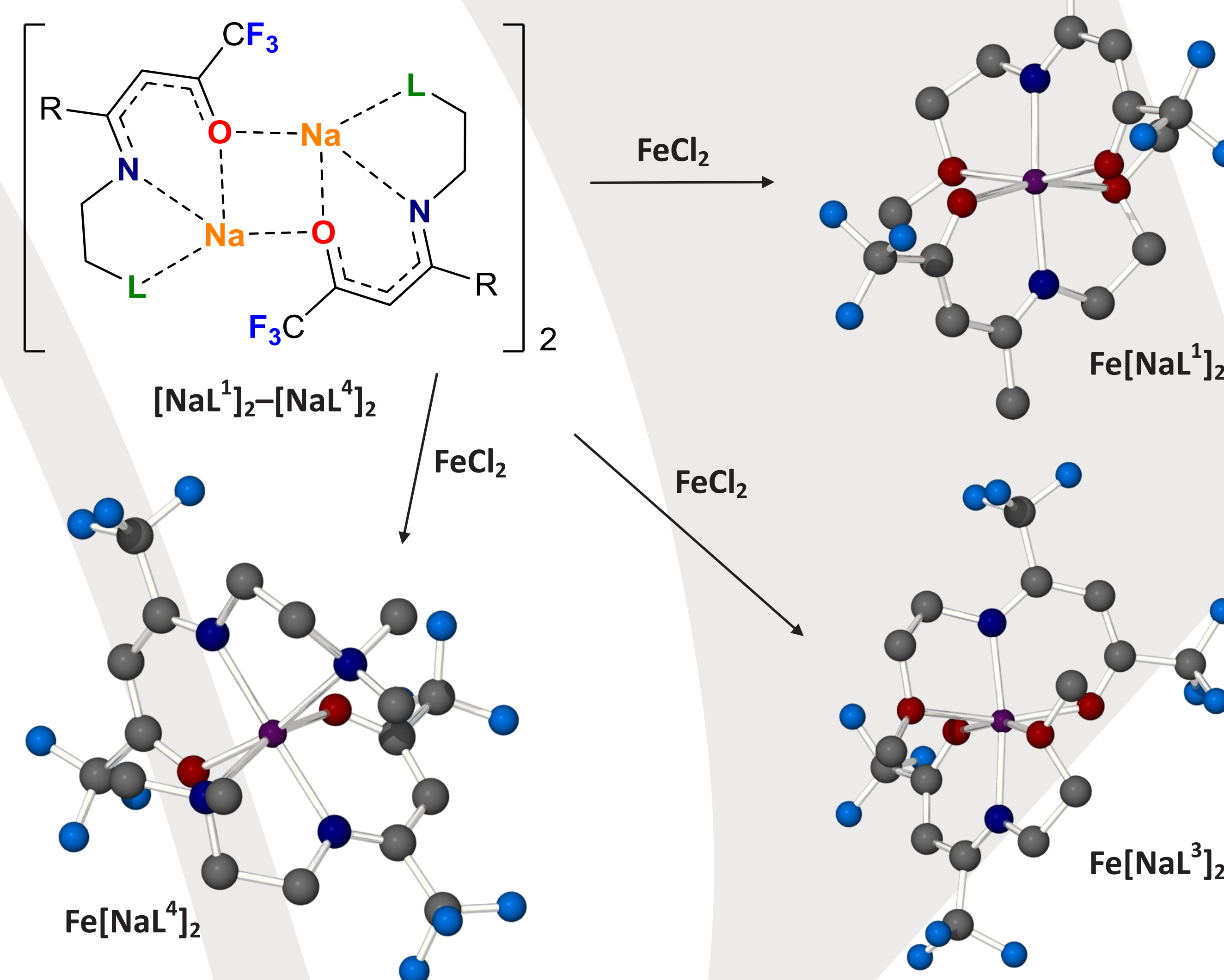


Fig. 5: Crystal structures of 3 iron (II) complexes (purple = iron, light blue = fluorine)

## Ligand synthesis

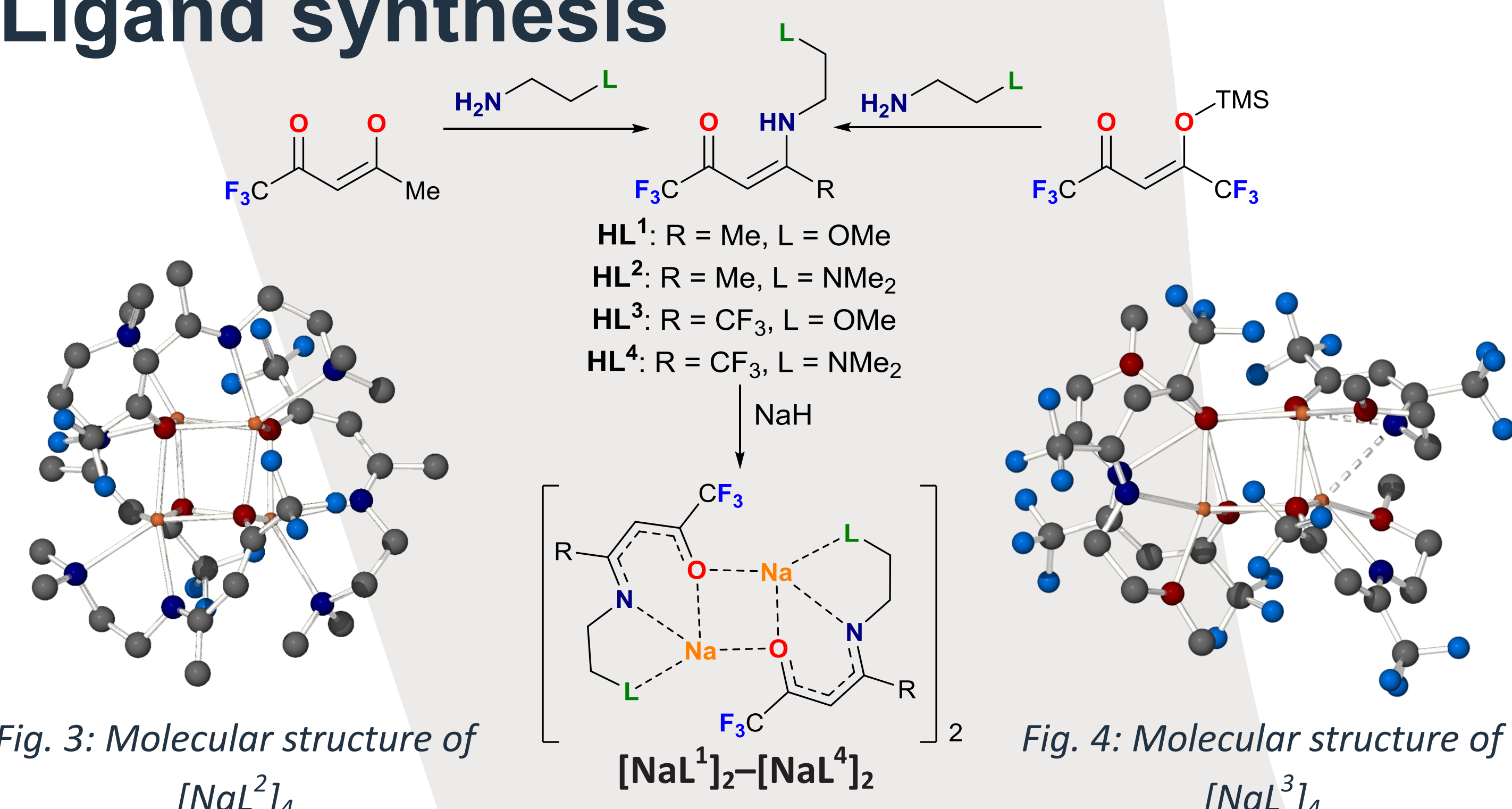
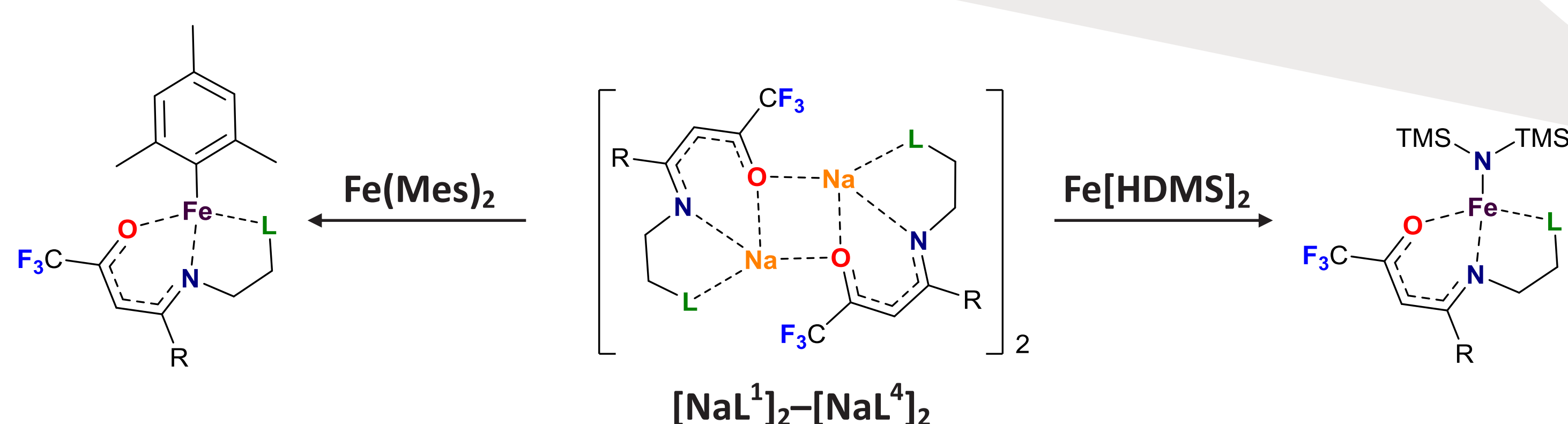


Fig. 3: Molecular structure of [NaL<sup>2</sup>]<sub>4</sub>

Fig. 4: Molecular structure of [NaL<sup>3</sup>]<sub>4</sub>

## Future work

- A second series of mono-substituted iron (II) complexes will be synthesised using the ketoiminate ligands we have developed.



- Synthesised hematite precursors will be analysed using thermogravimetric analysis.
- Based on the decomposition observed by thermogravimetric analysis, lead precursors will be chosen for deposition by AA-CVD.
- Hematite thin-films will be produced and fully characterised.
- Devices will be manufactured and tested for photoelectrochemical water-splitting.

## Conclusions

- A series of ketoiminate ligands and their sodium complexes have been synthesised and fully characterised.
- From the sodium salts, a series of potential single-source precursors for hematite have been synthesised and fully characterised.

## References

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